

Docket No.: H0610.0354/P354  
(PATENT)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of:  
Sven I. Hommeltoft, et al.

Application No.: 10/673,372

Filed: September 30, 2003

Art Unit: N/A

For: METHOD FOR THE RECOVERY OF  
PERFLUORINATED SULPHONIC ACID

Examiner: Not Yet Assigned

**CLAIM FOR PRIORITY AND SUBMISSION OF DOCUMENTS**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

Applicant hereby claims priority under 35 U.S.C. 119 based on the following prior foreign application filed in the following foreign country on the date indicated:

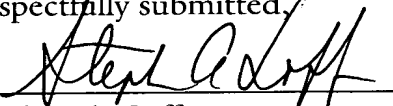
<u>Country</u>	<u>Application No.</u>	<u>Date</u>
Denmark	PA 2002 01622	October 25, 2002

In support of this claim, a certified copy of the said original foreign application is filed herewith.

Dated: November 10, 2003

Respectfully submitted,

By

  
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# Kongeriget Danmark

Patent application No.: PA 2002 01622  
Date of filing: 25 October 2002  
Applicant:  
(Name and address) Haldor Topsøe A/S  
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Denmark

Title: Fremgangsmåde til genvinding af perfluorinerede sulfonsyrer.

IPC: C 07 C 303/44; B 01 J 27/32; C 07 C 309/06

This is to certify that the attached documents are exact copies of the above mentioned patent application as originally filed.



**Patent- og Varemærkestyrelsen**  
Økonomi- og Erhvervsministeriet

22 October 2003

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**Modtaget**

**25 OKT. 2002**

**PVS**

24 October 2002

DK380-7237003

HABS/AKN

**Method for the recovery of perfluorinated sulphonic acid**

### FIELD OF THE INVENTION

The present invention relates to recovery of spent per-  
fluorinated sulphonic acid and in particular spent per-  
5 fluorinated sulphonic acid catalyst from residue in alkyla-  
tion of paraffins with olefins.

### BACKGROUND OF THE INVENTION

10 Perfluorinated sulphonic acids are effective catalysts in  
the alkylation of a paraffinic feedstock with olefinic al-  
kylation agents such as alkylation of isobutane with pro-  
pene and butenes as described in US patent Nos. 5,220,095,  
5,245,100 and 5,498,820. The alkylation process typically  
15 produces various amounts of spent acid catalyst. By-  
products formed in the alkylation reaction deactivate the  
spent acid.

To improve process economy of the processes involving per-  
20 fluorinated sulphonic acid catalysts it is highly desirable  
to recover spent acid catalyst and recycle the catalyst in  
its active form.

Several attempts have been made in the past to recover  
25 valuable amounts of spent perfluorinated sulphonic acid  
catalyst from alkylation residues. US Patent No. 6,340,414  
thus discloses recovery of spent acid by heating and dis-  
tillation. Recovery of a fluorinated sulphonic acid from a  
spent acid product by steps of subjecting the spent acid  
30 product to thermal treatment to obtain the acid in its ac-  
tive form and a residue and separating the active acid from  
the residue by stripping with a stripping agent and sepa-

rating the stripping agent from the active acid by distillation is known from EP-A-1,044,963.

5 By the above known recovery processes still valuable amounts perfluorinated sulphonic acid is contained in a viscous residue being formed during recovery.

10 DK PA 2001 00809 discloses a method to treat such viscous residues for the further recovery of acid by adding an alkyl ammonium salt of the acid to be recovered and subsequently extraction of the acid.

15 Viscosity of the residues increases as the acid is extracted. In some cases the organic part of the residue even solidifies and encapsulates the acid. The method of DK PA 2001 00809 therefore requires vigorous agitation and heating of the residue during extraction of the acid.

#### **SUMMARY OF THE INVENTION**

20

We have observed that addition of a hydrocarbon solvent being rich in aromatic compounds improves aqueous extraction of perfluorinated sulphonic acids from a residue being formed use or recovery of the acids as catalyst in alkylation of paraffins.

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Accordingly, this invention provides a method for the recovery of a perfluorinated sulphonic acid from an organic viscous residue by aqueous extraction of the acid from the residue in presence of a solvent mixture, which is rich in aromatic compounds.

30

Essentially, any hydrocarbon fraction being rich in aromatic compounds is useful in the inventive process. Light cycle oil, which is a by-product from fluid catalytic cracking of heavy oil, is an example of such a hydrocarbon fraction. Another useful hydrocarbon fraction is reformat gasoline. These fractions contain a mixture of hydrocarbons with a substantial amount of aromatic compounds.

#### DETAILED DESCRIPTION OF THE INVENTION

Spent acid from alkylation of paraffin alkylation in presence of trifluoromethanesulphonic acid was used in the following examples containing about 70% by weight trifluoromethanesulphonic acid and 30% by weight acid soluble oil (alkylation residue). The spent acid was mixed with 20% by weight triethyl ammonium triflate and then stripped in a stripping column with pentane at 250°C. Most of the acid in the spent acid was recovered in the overhead product from this stripping operation. An organic viscous residue was withdrawn from the bottom of the stripping column. The stripping residue was isolated and employed in the following experiments. The residue contained the entire amount of triethyl ammonium triflate and about 10% by weight of the amount of trifluoromethanesulphonic acid contained in the spent acid.

##### Example 1

Extraction of stripping residue in presence of reformat.

The extraction procedure was performed at room temperature and at atmospheric pressure. 35g of the residue were mixed with 15% by weight reformat and extracted five times with

50g portions of water by shaking for 30 seconds. An aqueous extract was separated from the residue by centrifugation. The content of recovered trifluoromethanesulphonic acid in each extraction is summarised in Table 1 below.

5

After five extractions the residue was extracted with diluted NaOH. Substantially no trifluoromethanesulphonic acid was found in the basic extract.

10 The above procedure was repeated. Results of the second experiment are listed in the Table below.

**Table 1**

Extraction of residue with water  
in the presence of reformat

15

Extraction	1 <sup>st</sup> experiment % recovery of tri- fluoromethanesul- phonic acid	2 <sup>nd</sup> experiment % recovery of tri- fluoromethanesul- phonic acid
1	95.8	91.0
2	3.53	7.95
3	0.61	0.95
4	0.06	0.04
5	0.01	0.02
Total extracted	100.0	100.0

### Example 2

20 Extraction of stripping residue in presence of light cycle oil (LCO).

Extraction of the residue was carried out by the same procedure as in the above Example 1. Results from two experiments are summarised in Table 2. NaOH extract in these ex-

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periments contained 0.1-0.2% by weight of the total amount of trifluoromethanesulphonic acid contained in the residue.

**Table 2**

5

Extraction	1 <sup>st</sup> experiment % recovery of tri- fluoromethanesul- phonic acid	2 <sup>nd</sup> experiment % recovery of tri- fluoromethanesul- phonic acid
1	82.4	81.4
2	14.96	16.51
3	1.46	1.21
4	0.53	0.22
5	0.48	0.60
Total extracted	99.8	99.9

**Comparison Example 3**

50g of the residue were mixed with 50g water. The extrac-  
 10 tion was performed at room temperature causing the residue  
 to be solidified, so that extraction and phase separation  
 were not possible.

**Example 4**

15 Extraction of residue with anisole.

Residue feed in this experiment did not contain triethylam-  
 monium triflate and consisted of trifluoromethane sulphonic  
 acid dissolved in a highly viscous organic residue. The  
 20 residue was dissolved in anisole (methylphenyl ether, meth-  
 oxybenzene) to form a 20% solution and 5g of this solution  
 was extracted with 5g water by shaking the two phases in a  
 centrifuge glass and subsequently separating the phases by  
 centrifugation. The aqueous phase was separated and the re-  
 25 maining organic phase was subsequently extracted with addi-



tional 5g portions of water. The analysis showed that 70% of the trifluoromethansulphonic acid was extracted in the first extraction, a further 21% were extracted in the second extraction and 5% were extracted in the third extraction. The remaining 4% were extracted in 3 subsequent extractions.

**CLAIMS**

1. Method for the recovery of a perfluorinated sul-  
phonic acid from an organic viscous residue by aqueous ex-  
5 traction of the acid from the residue in presence of a sol-  
vent containing one or more aromatic compounds.
2. Method according to claim 1, wherein said solvent  
comprises an aromatic ether solvent.
- 10 3. Method according to claim 2, wherein said aromatic  
ether is anisole.
4. Method according to claim 1, wherein said solvent  
15 is a hydrocarbon solvent containing 20% or more of aromatic  
hydrocarbons.
5. Method of claim 1, wherein the solvent is reformat  
gasoline.
- 20 6. Method of claim 1, wherein the solvent is light cy-  
cle oil.
7. Method according to any one of the preceding  
25 claims, wherein the perfluorinated sulphonic acid is tri-  
fluoromethanesulphonic acid.

**ABSTRACT**

Method for the recovery of a perfluorinated sulphonic acid  
from a viscous organic residue by aqueous extraction of the  
5 acid from the residue in presence of a solvent containing  
aromatic compounds.

Modtaget  
25 OKT. 2002

PVS

## OVERDRAGELSE

Undertegnede,

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**"Fremgangsmåde til genvinding af perfluorinerede sulfonsyrer"**

for hvilken ansøgning om patent er indleveret i Danmark til


Haldor Topsøe A/S  
Nymøllevej 55  
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således at samme må disponere herover.

Vederlaget for den overdragne ret overstiger ikke kr. 50.000,00.

Kgs. Lyngby, den 22 oktober 2002

  
Sven Ivar Hommeltoft

  
Ole Stahl